

Soft X-Ray Emission and Absorption Spectra in the Si *L* Region of Polysilanes

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Substituted polysilanes, (SiRR')_n, have attracted significant attention because of their unique electronic properties. Their characteristic electronic nature arises from band edge structures which are composed of valence and conduction bands from σ and σ^* bands, respectively, which differ from the electronic structure of polyacetylene. To further understand their electronic properties, we have measured the Si *L* x-ray emission spectra of a number of polysilanes with alkyl and phenyl substituents. In addition, their x-ray absorption spectra have also been measured to obtain information regarding unoccupied electronic orbitals.

Chemically synthesized polysilanes, (SiR₂)_n, where R indicates substitution with a methyl (Me; CH₃), ethyl (Et; C₂H₅), propyl (Pr; n-C₃H₇), butyl (Bu; n-C₄H₉), pentyl (Pe; n-C₅H₁₁) or phenyl (Ph; C₆H₅) group, were used for spectroscopic measurements. Soft x-ray emission spectra in the Si *L* region were measured using a grating x-ray spectrometer installed in the undulator beamline, BL-8.0.1. The photon energy of the monochromatized incident beam was tuned to about 130 eV to effectively excite Si2p-electrons while preventing multiple ionizations. Total-electron-yield (TEY) x-ray absorption spectra were obtained by monitoring sample photocurrent in BL-6.3.2. Measured x-ray emission and absorption spectra were analyzed using discrete variational (DV)-X α molecular orbital calculations.

Figure 1 shows soft x-ray emission and absorption spectra in the Si *L* region of both the polysilanes and the reference compounds, Si and SiO₂. In the emission spectra, polysilane spectral features exhibited similar structures; a main peak near 90 eV, and high-energy and low-energy shoulders clearly differ from those of the Si and SiO₂ references. In absorption spectra, alkyl-substituted polysilanes exhibit a threshold energy of 101 eV, while the Ph-substituted polysilane exhibits a slightly lower threshold energy. In the fine-structure at the thresholds of polysilanes, a pre-edge peak is observed near 101 eV and an intense peak is seen at 102 eV for the Ph-substituted polysilane. No such pre-edge or intense peaks, however, are observed in the spectra of alkyl-substituted samples. From spectral analysis using DV-X α molecular orbital calculations Si *L* x-ray emission spectra, which include a main peak with high- and low-energy shoulders, are explained by the summed DOS spectra of occupied Si3s and Si3d orbitals hybridized with Si3p, C2s and C2p orbitals. X-ray absorption spectra are also qualitatively explained by the summed DOS spectra of unoccupied Si3s and Si3d orbitals. In both x-ray emission and absorption spectra, little difference is observed among alkyl-substituted polysilanes. It is therefore confirmed that the length of alkyl substituents has little effect on the electronic structure of the Si backbone. X-ray spectral features of the Ph-substituted polysilane, however, slightly differ from alkyl-substituted features. This is explained by the difference in hybridization of Si and C orbitals between sp²-C atoms in phenyl substituents and sp³-C atoms in alkyl ones.

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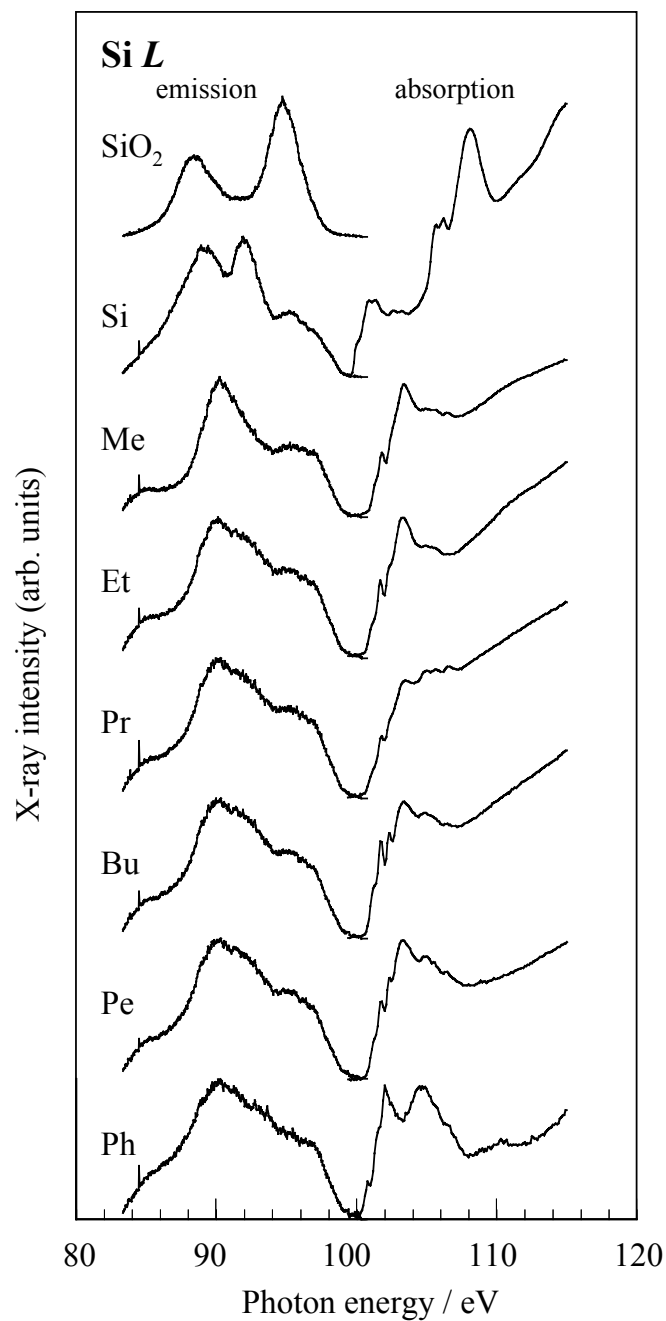


Figure 1 Soft x-ray emission and TEY x-ray absorption spectra in the Si *L* region of the polysilanes, (SiR₂)_n, and Si and SiO₂ reference compounds. Substituents in the polysilanes, R, are denoted by Me (CH₃), Et (C₂H₅), Pr (n-C₃H₇), Bu (n-C₄H₉), Pe (n-C₅H₁₁), and Ph (C₆H₅).